METAL OCCURRENCE AND TEXTURAL-COMPOSITIONAL PROPERTIES IN BOTTOM SEDIMENTS FROM RIGHT MARGIN TRIBUTARIES OF THE LOWER DEL PLATA BASIN

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Abstract: Sediment metal geochemistry from different surface water basins of South America has recently started to be investigated, together with textural properties of transported materials. The objective of the present study is to analyze and compare the metal contents in bottom sediments from down-stream positions of eight drainage basins running across eolic and water-reworked substrate materials from the Pampean loess, in relation to matrix composition, stream location and geomorphology from a relevant area of the del Plata basin. The sector, under the influence of extensive crop agriculture, holds more than half of Argentina’s population and the largest country industrial settings. Sampling, included extraction of cores (25 cm average recovery) from both margins at a 50 cm water-depth, from equivalent distal positions of different fluvial basins of the Undulated Pampa discharging into the Paraná river (del Medio, Ramallo, Tala, Arrecifes, Areco), were analyzed and also compared with those discharging into the Río de la Plata estuary (Carnaval-Martín, del Gato and del Pescado). A comparison with selected upstream positions was also included. Standardized methods for the determination of granulometric parameters, clay mineral composition, and metal contents were employed. Assessment of differences between rivers and metal content was done by ANOVA-MANOVA. Dot plot diagrams were used to observe distribution and trends of metal contents and matrix components. Almost 50% of samples fall in the mud and sandy mud sediment classification, and the majority of the rest in sandy silt field. Distal sediments from the northern sector show lower clay and organic matter contents than the southern sector rivers. Illite is the main clay component in all streams. Smectite and kaolinite levels are also high in streams flowing to the Río de la Plata. Metal contents indicate that Fe and Mn concentrations are very variable. The order of abundance for all studied metals, considering raw mean contents, is Fe>Mn>Pb>Cu>Cr>Ni>Cd, with lower mean values in the northern sector streams. Comparisons between clay, organic matter, and raw metal contents show significant correlations with most metals only for the northern streams. Statistical analysis with ANOVA-MANOVA between streams, metal contents, and stream locations indicate significant differences between all streams (p < 0.0000) for all metals (raw and grain size normalized data for clay and also silt plus clay). The comparison of streams from the northern sector shows no significant differences (p < 0.000) between them, with both raw and normalized metal contents. Cluster analysis shows the presence of two main clusters grouping both stream sectors. We can conclude that the northern sector streams are significantly similar and are in correspondence with a higher homogeneity of provenance materials along the courses. On the contrary, the southern streams are more variable, especially considering a different depositional environment in their distal positions. Also, a higher influence of antropic activities could be observed in this sector. Control of metal-polluted sites could be introduced taken into
BACKGROUND

Compositional studies of suspended matter in water from rivers have revealed that the fine fraction reflects either substrate lithology from source areas or account existent experience in sediment management programs and local projects for the protection of the Río de la Plata estuary under bilateral agreement between Argentina and Uruguay.

Keywords: streambed sediments, metal content, textural properties, clay minerals, lower Paraná-Río de la Plata
margin of the Paraná River and the Río de la Plata estuary in South America has recently started in relation to its sedimentology, mineralogy, and geochemistry. Previous studies have focused on the analysis of the distribution patterns of heavy metals in sediments from restricted sectors of the system (Villar et al., 1998, 1999; Cataldo et al., 2001; Ronco et al., 2001; Camilion et al., 2003a). The present contribution studies the content of metals in bottom sediments from down-stream positions of eight drainage basins running across Pampean loess, eolic, and water-reworked substrate materials. Two main sectors with different geomorphological and soil characteristics and productive activities were analyzed and compared. A northern sector, with water streams discharging in the lower Paraná River, associated to extensive agriculture; and a southern sector, heavily populated and industrialized, from the coast of the Río de la Plata estuary. Clay mineral and grain size composition, metal concentration, metal matrix correlations, and comparisons between streams and stream sectors are analyzed.

**METHODS**

**Study area**

Sampling of bottom sediments using 4 cm diameter plastic tubes -n = 41, including 20 samples from previous published data set (Ronco et al., 2001),- was done in equivalent distal positions, (both margins) of the different fluvial basins of the Undulated Pampa of Argentina (Manassero et al., 2004; Dangavs, 2005), and also in an upstream position of a selected stream for comparison between sectors. Water depth at the sampling site was between 0.5 and 1 m, and sediment depth core recovery was within 30 cm. The studied rivers

![Figure 1. Map of the study area, streams, and sampling point locations. Open triangles show sampling point locations.](image)
(Fig. 1) flow from the southwest to the northeast discharging into the Paraná river (northern sector streams: del Medio, Ramallo, Tala, Arrecifes, Areco) (Manassero et al., 2004) and the Río de la Plata estuary (southern sector streams: Carnaval-Martín, Del Gato, Del Pescado) (Ronco et al., 2001; Camilion et al., 2003a). The northern group stream run across sandy silt materials of the Buenos Aires Formation (Dangavs, 2005) along the entire course, while the southern group only run this formation in the upper and/or middle topographic sectors, and then on a coastal plain of Holocene marine fine materials (Ronco et al., 2001; Manassero et al., 2004).

Sedimentological and chemical analysis

Granulometric analysis was performed by sieving and settling velocity technique at one interval (Day, 1965). Grain size classification of sediments was made according to Folk (1954). The clay fraction was analyzed by X-ray diffraction on normal, glycolated, and calcinated sample (Moore and Reynolds, 1989). Organic matter content was determined according to Walkey and Black (Allison, 1965). Analysis of total Cr, Ni, Cu, Zn, Cd, Pb, Fe, and Mn content was done by atomic absorption spectrometry following acid digestion of samples (USEPA, 1986; APHA, 1998). Quality controls included reagent blanks, duplicate samples (APHA, 1998), analysis of certified reference material (Pond Sediment, National Institute for Environmental Studies, Tsukuba Ibaraki, Japan), and traceable reference standards (AccuStandard, Inc.).

Statistical analysis

Statistical analysis of results was done by ANOVA and regression analysis to assess the differences between rivers and raw and normalized metal contents (Horowitz, 1985; Trimble and Hoenstine, 1997). Dot plot diagrams are given to observe distribution and trends of metal contents and matrix components. Cluster analysis using Euclidian distances and single linkage for raw metal contents and clay proportion as variables and sampling sites was also performed.

RESULTS

Regarding matrix properties, granulometric analysis indicates that almost 50% of samples fall in the mud and sandy mud sediment classification, and the majority of the rest in sandy silt field (Folk, 1954). Sediments from the northern sector show relatively lower clay contents (mean content, 30.2%) when compared to the southern sector rivers (mean content, 53.9%), with the exception of the upper stream sampling sector of the Arrecifes, which is similar to the second group (Fig. 2).

Organic matter and total clay content has been plotted in Fig. 3. Organic matter concentrations vary between 0.2 to 4.2% with higher mean values in the Arrecifes tributary and the Del Gato stream. A high variation in the proportion of clay content levels is observed for all streams (from 4.4 to 72.6%). The southern streams, together with the Arrecifes river and its tributary, are richer in clay. This result can also be observed in figure 2. The majority of the Northern streams fall within the sandy silt and sandy mud and muddy sand, while most of the southern streams and the tributary fall in the mud classification.
In a similar manner, as seen for the total clay content, compositional differences related to clay mineral groups were observed between regions (Fig. 4). Illite, from loessic eolic substrate regional provenance, is the main clay component in all studied streams. The streams flowing to the Río de la Plata margin also show high levels of smectite and kaolinite. The clay mineral associations from the northern area correspond to continental wind-blown fine material, while in the southern streams a mixture of provenances is found. Added to the eolic illite, both smectitic marine Holocene clay and recent kaolinitic inputs from the del Plata basin are also found (Ronco et al., 2001; Manassero et al., 2004).

With respect to metal composition, results show that the concentration of Fe and Mn (mg/Kg dry weight) is very variable (Fig. 5) (Fe: average for all streams, 26596.6 and SD 16434.9; Mn: average for all streams, 698.3 and SD 834.0; n=41), with lower mean values in the northern sector area when considering all distal positions. The raw mean contents of the other metals (mg/Kg dry weight) (Fig. 6) in all streams (with standard deviation in parenthesis for n=41) in order of abundance are as follows: Zn, 95.74 (173.79); Pb, 37.02 (53.57); Cu, 33.15 (31.14); Cr, 24.79 (18.66); Ni, 14.71 (9.06); Cd, 0.67 (0.32). The northern sector streams (n=21) exhibit lower contents: Zn, 34.08 (15.40); Pb, 20.46 (26.01); Cu, 21.71 (16.09); Cr, 15.99 (8.26); Ni, 6.4 (3.7); Cd, 0.57 (0.17). For the case of the Arrecifes tributary, the mean Ni content is three times the northern average, assimilating to the southern streams.

Comparisons between clay, organic matter, and raw metal contents with all data sets show significant correlations ($\alpha=0.05$ in all tests), only between clays and Ni (r: 0.59, n=36), and organic matter and Mn (r: 0.42, n=28). The same analysis, when considering the data set for the northern streams, shows significant correlations between clay and Cr, Ni, Zn, Fe, and Pb contents (r values: 0.61, 0.60, 0.70, 0.45, and 0.44, respectively, for n=21), and organic matter and Mn, Cr, Ni, Zn, Cu, and Pb (r values: 0.69, 0.73, 0.64, 0.78, 0.71, and 0.77, respectively, for n=12). The Fe content also show significant correlation with the rest of the metals for all streams (r values: Cr, 0.68; Ni, 0.60; Cd, 0.36; Zn, 0.52; Cu, 0.59; Pb, 0.60; with n=41 for Cr, Cd, Zn, Cu, Pb, and n=36 for Ni), except for Mn; and for the northern...
Comparisons by statistical analysis with ANOVA-MANOVA between streams, metal contents, and stream locations indicate significant differences between all streams ($p < 0.0000$) for all metals (raw and grain size normalized data for clay and also silt plus clay). Although, the comparison of streams from the northern sector shows no significant differences ($p < 0.000$) between them for either raw or normalized metal contents. When analyzing the effect of the metal content, the influence of Fe on data can be observed, being the major measured component of the matrix with a variable concentration. This behavior is valid for all streams. Clay-normalized metal data shows that El Tala is significantly different ($p < 0.05$) from the rest of the streams due to a very low clay level.

The dendrogram summarizing the three main clusters identified using average linkages is presented as Fig. 7. One of the clusters corresponds to the northern sector streams, including the Arrecifes tributary, except for one site in a small wetland, resolved in a second cluster, together with the southern streams. A smaller cluster is identified for some of the samples of the Carnaval-Martin stream, associated with distinctively low concentrations of iron.

**DISCUSSION**

In general, the observation of differences between grain size populations (Fig. 2) indicates predominance of saltation and suspension processes. Although all streams show similar patterns of grain size distribution, El Tala exhibits the presence of high silt content (95%) and smectitic clay (Fig. 3 and 4), probably due to the composition of source-substrate materials (mainly wind driven sediments) or the washing – reworking effect. When analyzing the northern streams, the Arrecifes shows a loss of clay particles and organic matter between source and distal positions, indicating the presence of siltation in this watercourse (Camilion et al., 2003b). This process does not seem to prevail in the southern coast streams of the Río de la Plata area due to the smaller size of their basins and also the existence of a wide marshy coastal plain where the streams flow into. Data from a previous study show higher clay predominance in distal stream positions (Ronco et al., 2001). Differences in the sedimentary processes could be explained by transport and depositional conditions, added to particular lithogeological and morphological characteristics, with an estuarine lower plain, where higher deposition of fine materials occurs in the southern sector. Clay composition, with higher proportion of smectite, in stream sediments of the coastal plain is also related to inherited substrate lithology from an older marine depositional system (Camilion et al., 2003a; Cavalloto et al., 2005).

There is a distinctive grouping tendency between northern and southern stream distal positions, with higher similarities in metal content levels within the first group, and better correlations with main matrix components. Although, the upstream sector of the Arrecifes river shows characteristics from both groups. Some streams flowing to the coastal area of the Río de la Plata present metal pollution in down-stream positions associated to point and non-point sources form urban, industrial, and agricultural activities. Particu-
Figure 6. Variability of raw minor metal content (mg/Kg) per stream. a: del Medio; b: Ramallo; c: Tala; d: Arrecifes; e: Areco; f: Arrecifes tributary; g: Carnaval-Martin; h: del Gato; i: Pescado.

Figure 6. Variabilidad del contenido sin normalizar de metales minoritarios (mg/Kg) para cada curso de agua. a: del Medio; b: Ramallo; c: Tala; d: Arrecifes; e: Areco; f: Arrecifes tributary; g: Carnaval-Martin; h: del Gato; i: Pescado.

larly, del Gato stream shows metal polluted sediments in its middle sector (Ronco et al., 2001), also in relation to neighboring soils (Camilion et al., 2003a). A high variability in the content of Fe and Mn indicates differences in physicochemical depositional environments. In the coastal plain, with dominant chemical and biochemical redox processes producing Fe and Mn neoformations (Ronco et al., 2001), presence of local hydromorphic conditions and alkaline soils (Camilion et al., 2003a), higher concentrations are observed. This is also in agreement with higher proportions of imported kaolinite (from estuary inputs), a clay mineral associated in the mobilization or precipitation of both metals (Pracejus and Bolton, 1992). The cluster analysis complements the above observations, indicating two major groupings belonging to the two different environments.

A comparison of metal contents in bottom sediments
from the distal positions of all of the studied streams shows that they are within the concentrations levels of those reported for sediments near the coasts of the Río de la Plata and low Paraná river (Villar et al., 1998, 1999). However, the concentration levels of Cr, Pb, Zn, Cd, and Cu are, respectively, 100-, 20-, 10-, 8-, and 2-fold lower than those reported for a very highly polluted stream running across the metropolitan area of Buenos Aires (Kreimer et al., 1996) and flowing into the Río de la Plata coast in an intermediate position between the two studied stream groups. Also, mean concentrations of Cr were almost one order of magnitude lower than those reported for the Delta region by Cataldo et al. (2001).

CONCLUSIONS

The results of this study show that metal distribution trends in distal positions from right margin tributaries of the Lower del Plata Basin correspond with the two main lithogeological sectors and depositional environments. Metal contents in the system exhibits good correlations with matrix components like fines, organic matter and colloids. Also, changes due to human activities indicate metal compositional variations, with higher concentration levels close to very urbanized and industrialized areas. Site-specific management of polluted sectors within a framework of conceptual river basin scale (Apitz and White, 2003; Owens, 2005) could be recommended for this basin sector. Perspective of future studies on metal provenance, flows, and budgets should take into account the previous experience in several countries on sediment management programs (Köthe 2003), and regional projects carried under country bilateral agreements for the environmental protection of the Río de la Plata and its maritime front, FREPLATA (Project PNUD/ GEF/ RLA/ 99/ G31; www.freplata.org).

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